

Harmonium as a laboratory for mathematical chemistry

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Abstract

Thanks to an algebraic duality property of reduced states, the Schmidt best approximation theorems have important corollaries in the rigorous theory of two-electron molecularae. In turn, the “harmonium model” or “Moshinsky atom” constitutes a non-trivial laboratory bench for energy functionals proposed over the years (1964–today), purporting to recover the full ground state of the system from knowledge of the reduced 1-body matrix. That model is usually regarded as solvable; however, some important aspects of it, in particular the exact energy and full state functionals—unraveling the “phase dilemma” for the system—had not been calculated heretofore. The solution is given here, made plain by working with Wigner quasiprobabilities on phase space. It allows in principle for thorough discussions of the merits of several approximate functionals popular in the theoretical chemical physics literature; in this respect, at the end we focus on Gill’s “Wigner intracule” method for the correlation energy.

1 Introduction

At the heart of theoretical chemistry sits the Coulson program of replacing the wave function by the (reduced) 12-variable 2-body matrix ρ_2 [1]. For this function of twelve variables the basic energy functional is trivially

known. Unfortunately, the N -representability problem for ρ_2 has never been solved in an usable way. Density functional theory (DFT) was unleashed by the Hohenberg–Kohn discovery that somehow the same information as in the wave function or in the 2-matrix is stored in the humble 3-variable electronic density. However, the energy functional encoding such information is unknown, and must have strangely non-local properties—in relation with the existence of negative ions, for instance [2]. A natural alternative is the Gilbert program [3] based on the 6-variable 1-body matrix ρ_1 , for which the N -representability question is solved.¹

Now, possession of the 1-body matrix for an N -electronic system does not allow exact inference of the corresponding 2-body matrix ρ_2 , or of the correlation energy. It is natural to diagonalize ρ_1 and seek to expand ρ_2 in terms of eigenfunctions of ρ_1 (“natural orbitals”) and its eigenvalues $0 \leq \nu_j \leq 1$ (“occupation numbers”), with $\sum_j \nu_j = N$. Over the years, starting with the work by Müller [8], approximate relations between ρ_2 and ρ_1 and energy functionals based on this spectral analysis of ρ_1 have been suggested and tried, with various results.

Two-electron systems constitute an exception to our ignorance. For them it is feasible to a large extent to reconstruct ρ_2 from ρ_1 , and so fulfil the Coulson and Gilbert programs. As we shall recall, that it may be so stems simply from Schmidt’s approximation theorems [9]. For a reduced 1-density of the kind

$$\rho_1(\mathbf{x}, \mathbf{x}') = (\uparrow_1 \uparrow_{1'} + \downarrow_1 \downarrow_{1'}) \rho_1(\mathbf{r}, \mathbf{r}') = (\uparrow_1 \uparrow_{1'} + \downarrow_1 \downarrow_{1'}) \sum_j n_j \phi_j(\mathbf{r}) \phi_j^*(\mathbf{r}'),$$

¹After a long period of stasis, recently there has been progress on the representability problem for 2-matrices, and on pending questions of representability for 1-matrices [4–7].

with $\sum_j n_j = 1$, the corresponding 2-density matrix is given by

$$\begin{aligned} \rho_2(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}'_1, \mathbf{x}'_2) &= \frac{1}{2} (\uparrow_1 \downarrow_2 - \downarrow_1 \uparrow_2) (\uparrow_{1'} \downarrow_{2'} - \downarrow_{1'} \uparrow_{2'}) \\ &\times \begin{pmatrix} \phi_1(\mathbf{r}_1) & \phi_2(\mathbf{r}_1) & \phi_3(\mathbf{r}_1) & \cdots \end{pmatrix} \begin{pmatrix} c_1 & & & \\ & c_2 & & \\ & & c_3 & \\ & & & \ddots \end{pmatrix} \begin{pmatrix} \phi_1(\mathbf{r}_2) \\ \phi_2(\mathbf{r}_2) \\ \phi_3(\mathbf{r}_2) \\ \vdots \end{pmatrix} \\ &\times \begin{pmatrix} \phi_1^*(\mathbf{r}'_1) & \phi_2^*(\mathbf{r}'_1) & \phi_3^*(\mathbf{r}'_1) & \cdots \end{pmatrix} \begin{pmatrix} c_1^* & & & \\ & c_2^* & & \\ & & c_3^* & \\ & & & \ddots \end{pmatrix} \begin{pmatrix} \phi_1^*(\mathbf{r}'_2) \\ \phi_2^*(\mathbf{r}'_2) \\ \phi_3^*(\mathbf{r}'_2) \\ \vdots \end{pmatrix}. \end{aligned} \quad (1)$$

Alas, the recipe, although exact, is underdetermined: of the c_j we only know that $|c_j|^2 = n_j$. This is a “phase dilemma” of 1-body matrix functional theory. We work here only with states described by real wave functions: this still leaves us with an infinite number of signs to account for.

The harmonium model originally proposed by Moshinsky [10] consists of two spin- $\frac{1}{2}$ fermions trapped in a harmonic potential and repelling each other with a Hooke’s law force, as well. It constitutes an analogue to a two-electron atom, helpful to illustrate the main ideas of reduced density matrices and correlation energy in an exactly solvable context. Its ground state, as well as the reduced density matrix and the pair distribution, exhibiting correlation, are well known in the standard wave function formalism [11]. Recently, this model has been recruited for suggesting approximate Ansätze for correlation energy density [12], and other purposes [13].

Nevertheless, within the standard formalism it is not at all obvious how to go about the sign conundrum. We manage here to sidestep all the difficulties, and exemplify the two-electron state theorem for harmonium, by working with Wigner functions on phase space instead. Mathematically, Wigner phase space states are equivalent to density matrices, sporting of course the same number of variables. However, our approach calls for a different type of physical intuition, encapsulating some of the non-locality which is the bane of DFT.

Like one-body density matrix functional theory, Wigner functional theory sits midway between ordinary DFT and the Coulson proposal. Currently Gill and coworkers [14] pursue a vigorous program to understand correlation

energies via Wigner intracules: our method also sits transversally midway between the 6-variable Gilbert and Gill programs. We mention as well a different fusion of the Schmidt and Wigner ways, related to information theory [15], and a recent quantum phase space view of harmonium by Dahl [16].

The plan of the article: we start by recalling the classical contribution by Schmidt, with a pedagogical bent. We show how to derive from it the exact energy functional for two-electron systems, determined up to an unknown configuration of signs. After that, we describe harmonium by phase space methods; these provide the fast lane towards an elegant and complete description of this system. Finally, we examine Gill's Wigner intracule method for correlation energy from our results on harmonium.

2 Schmidt's theorem and its meaning for heliumalikes

Little more than singular value decomposition of matrices is involved here. Let $\Psi(x_1, x_2)$ be the wave function describing a pure state of any system with two electrons—including the helioid series, starting with H^- , He , and molecules like H_2 . For simplicity, and because in absence of magnetic fields this is actually the case for such systems, we assume that Ψ is real. Let us expand Ψ in suitable orthonormal basis (ONB), also taken real,

$$\begin{aligned} \Psi(x_1, x_2) &= \sum_{ij} \langle f_i h_j | \Psi \rangle f_i(x_1) h_j(x_2) =: \sum_{ij} f_i(x_1) c_{ij} h_j(x_2) \\ &:= \begin{pmatrix} f_1(x_1) & f_2(x_1) & f_3(x_1) & \cdots \end{pmatrix} C \begin{pmatrix} h_1(x_2) \\ h_2(x_2) \\ h_3(x_2) \\ \vdots \end{pmatrix}. \end{aligned}$$

Suppose the eigenvalue problem for the (real positive symmetric) matrix CC^t is solved by

$$CC^t u_j = \sigma_j^2 u_j.$$

We order the singular values: $\sigma_1 \geq \sigma_2 \geq \sigma_3 \geq \cdots \geq 0$. Then the u_j are the columns of an orthogonal matrix U . Define now $v_i = C^t u_i / \sigma_i$. These are at least partially the columns of another orthogonal matrix, say V , since

$$v_i^t v_j = \frac{\langle u_i | CC^t u_j \rangle}{\sigma_i \sigma_j} = \frac{\sigma_j^2 \langle u_i | u_j \rangle}{\sigma_i \sigma_j} = \delta_{ij}.$$

Add to them any orthonormal basis for $\ker C$. Notice moreover that

$$u_i^t C v_j = \frac{1}{\sigma_i} u_i^t C C^t u_j = \delta_{ij} \sigma_i, \quad \text{or} \quad U^t C V = \begin{pmatrix} \sigma_1 & & & \\ & \sigma_2 & & \\ & & \sigma_3 & \\ & & & \ddots \end{pmatrix} =: \Sigma.$$

We just have reached the singular value decomposition of (real) matrices:

$$C = U \Sigma V^t, \tag{2}$$

with Σ diagonal nonnegative and U, V orthogonal, whose columns are “singular vectors”, respectively left-hand and right-hand —see for instance [17, Chap. 5]. Notice the non-unicity of V .²

Before proceeding, we remark that Schmidt in [9] showed that the *best* finite-rank approximation (in the sense of any orthogonally invariant norm) to C is given simply by

$$C^{(k)} = U^{(k)} \Sigma^{(k)} V^{(k)t},$$

where $\Sigma^{(k)}$ is obtained just by cutting out $\sigma_{k+1} = \sigma_{k+2} = \dots = 0$, and $U^{(k)}, V^{(k)}$ are the matrices obtained by conformally keeping in U, V the first k singular vectors. Most important for us, we note as well that CC^t (save the conventional factor 2) precisely represents the 1-body density associated to Ψ :

$$\begin{aligned} \int \Psi(x, x_2) \Psi(x', x_2) dx_2 &= \sum_{ijk} f_i(x) c_{ij} c_{kj} f_k(x') = \sum_l \sigma_l^2 \phi_l(x) \phi_l(x') \\ &=: \sum_l (\nu_l/2) \phi_l(x) \phi_l(x') =: \frac{1}{2} \rho_1(x, x'); \end{aligned}$$

where we have made the spectral expansion of that density: the ν_l are the chemists’ *occupation numbers* and the ϕ_l the *natural orbitals*. We witness here a wonderful convergence of mathematical relevance and physical import. Schmidt approximation then implies that a state made out of $K(K-1)/2$ configurations can be rewritten with K configurations.

²This decomposition amounts to the canonical “Schmidt series” for an operator and the “Schmidt decomposition” of tensor products, currently taught to students interested in entanglement, decoherence and quantum information theories [18].

Going back to (2) and denoting:

$$V^t \begin{pmatrix} h_1 \\ h_2 \\ \vdots \end{pmatrix} = \begin{pmatrix} \varphi_1 \\ \varphi_2 \\ \vdots \end{pmatrix},$$

it is clear that $C^t C$ is the matrix representation of ρ_1 in the ONB $\{|h_j\rangle\}$ and CC^t the one in the ONB $\{|f_i\rangle\}$, and that

$$\begin{aligned} \Psi(x_1, x_2) &= \sum_i \pm \sqrt{\nu_i/2} \phi_i(x_1) \varphi_i(x_2) \\ &=: \sum_i \pm \sqrt{\nu_i/2} \phi_i(x_1) \int dx \phi_i(x) \Psi(x, x_2). \end{aligned}$$

The sign indetermination at this stage cannot be removed. The challenge is to identify the right configuration of signs for each system from energy considerations.

Since moreover Ψ is skewsymmetric, φ_i must be a natural orbital itself. For instance, for the singlet ground state of the helioids,

$$\Psi_{\text{gs}}(x_1, x_2) = \frac{1}{\sqrt{2}} (\uparrow_1 \downarrow_2 - \downarrow_1 \uparrow_2) \Psi(\mathbf{r}_1, \mathbf{r}_2),$$

if we choose

$$\begin{aligned} \phi_{2i-1}(x) &= \uparrow \phi_i(\mathbf{r}), & \phi_{2i}(x) &= \downarrow \phi_i(\mathbf{r}), \\ \text{then } \varphi_{2i-1}(x) &= \downarrow \phi_i(\mathbf{r}), & \varphi_{2i}(x) &= -\uparrow \phi_i(\mathbf{r}). \end{aligned}$$

For the triplet states we have:

$$\begin{aligned} \Psi_{\text{t1}}(x_1, x_2) &= \uparrow_1 \uparrow_2 \sum_i d_i [\gamma_i(\mathbf{r}_1) \omega_i(\mathbf{r}_2) - \omega_i(\mathbf{r}_1) \gamma_i(\mathbf{r}_2)]; \\ \Psi_{\text{t0}}(x_1, x_2) &= \frac{1}{\sqrt{2}} (\uparrow_1 \downarrow_2 + \downarrow_1 \uparrow_2) \sum_i d_i [\gamma_i(\mathbf{r}_1) \omega_i(\mathbf{r}_2) - \omega_i(\mathbf{r}_1) \gamma_i(\mathbf{r}_2)]; \\ \Psi_{\text{t-1}}(x_1, x_2) &= \downarrow_1 \downarrow_2 \sum_i d_i [\gamma_i(\mathbf{r}_1) \omega_i(\mathbf{r}_2) - \omega_i(\mathbf{r}_1) \gamma_i(\mathbf{r}_2)]; \end{aligned}$$

so, if we choose

$$\begin{aligned} \phi_{2i-1}^1(x) &= \uparrow \gamma_i(\mathbf{r}), & \phi_{2i}^1(x) &= \uparrow \omega_i(\mathbf{r}), \\ \text{then } \varphi_{2i-1}^1(x) &= \uparrow \omega_i(\mathbf{r}), & \varphi_{2i}^1(x) &= -\uparrow \gamma_i(\mathbf{r}); \end{aligned}$$

and similarly in the other cases.

The Schmidt theorem has a far-reaching generalization for best approximations of N -body wave functions in terms of orbitals of complementary reduced density matrices. A good place to see that in action is [11].

3 Harmonium on phase space

The Hamiltonian for harmonium in Hartree units is

$$H = \frac{p_1^2}{2} + \frac{p_2^2}{2} + \frac{k}{2}(r_1^2 + r_2^2) - \frac{\delta}{4}r_{12}^2. \quad (3)$$

Introduce extracule and intracule coordinates, respectively given by

$$\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/\sqrt{2}, \quad \mathbf{r} = (\mathbf{r}_1 - \mathbf{r}_2)/\sqrt{2},$$

with conjugate momenta

$$\mathbf{P} = (\mathbf{p}_1 + \mathbf{p}_2)/\sqrt{2}, \quad \mathbf{p} = (\mathbf{p}_1 - \mathbf{p}_2)/\sqrt{2}.$$

Therefore

$$H = H_R + H_r = \frac{P^2}{2} + \frac{\omega^2 R^2}{2} + \frac{p^2}{2} + \frac{\mu^2 r^2}{2}.$$

We have introduced the frequencies $\omega = \sqrt{k}$ and $\mu = \sqrt{k - \delta}$; for both particles to remain in the potential well, assume $\delta < k$.

The translation to phase space of the analysis in the previous section was accomplished in [19]. One could depart somewhat from the treatment in this reference, though. There, following in particular Springborg and Dahl [20], by outright transfer from the density matrix formalism, we regard the 1-body and 2-body Wigner functions defined below as respectively $2 \times 2, 4 \times 4$ matrices. It is however more natural, as advised by Wigner himself [21] and effected in [22], to describe spin by combining row and column components to have simpler transformation properties; these are none other than the ones corresponding to the tensor representations of the rotation group. In particular for the reduced 1-density for a two-electron system in a singlet spin state, the spin factor:

$$\frac{1}{2}(\uparrow_1 \uparrow_{1'} + \downarrow_1 \downarrow_{1'})$$

is just the identity scalar, and can be omitted. In general, for the 1-body Wigner function one organizes the spin factors in terms of the Cartesian components of the spin operator vector.

We may concentrate on the spinless part of the ground state henceforth. In general, the spinless Wigner quasiprobability (normalized to one) corresponding to a (real) 2-particle wave function Ψ is given by

$$\begin{aligned} P_\Psi(\mathbf{r}_1, \mathbf{r}_2; \mathbf{p}_1, \mathbf{p}_2) \\ = \frac{1}{\pi^6} \int \rho_2(\mathbf{r}_1 - \mathbf{z}_1, \mathbf{r}_2 - \mathbf{z}_2; \mathbf{r}_1 + \mathbf{z}_1, \mathbf{r}_2 + \mathbf{z}_2) e^{2i(\mathbf{p}_1 \cdot \mathbf{z}_1 + \mathbf{p}_2 \cdot \mathbf{z}_2)} d^3 z_1 d^3 z_2, \end{aligned} \quad (4)$$

with $\rho_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) = \Psi(\mathbf{r}_1, \mathbf{r}_2) \Psi(\mathbf{r}'_1, \mathbf{r}'_2)$. The definition extends to transition matrices $|\Phi\rangle\langle\Phi'|$ as well:

$$\begin{aligned} P_{\Phi\Phi'}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{p}_1, \mathbf{p}_2) \\ = \frac{1}{\pi^6} \int \Phi(\mathbf{r}_1 - \mathbf{z}_1, \mathbf{r}_2 - \mathbf{z}_2) \Phi'(\mathbf{r}_1 + \mathbf{z}_1, \mathbf{r}_2 + \mathbf{z}_2) e^{2i(\mathbf{p}_1 \cdot \mathbf{z}_1 + \mathbf{p}_2 \cdot \mathbf{z}_2)} d^3 z_1 d^3 z_2. \end{aligned}$$

For harmonium the Wigner distribution factorizes into extracule and intracule parts:

$$P_{\text{gs}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{p}_1, \mathbf{p}_2) = \frac{1}{\pi^6} \exp\left(-\frac{2H_R}{\omega}\right) \exp\left(-\frac{2H_r}{\mu}\right). \quad (5)$$

This is reached most efficiently and elegantly by the methods of phase space quantum mechanics [23]. One can now obtain ρ_2 by the inverse formula of (4)—easily provided for by Fourier analysis. The pairs density $\rho_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_2)$ is recovered by integration over the momenta.

The reduced 1-body phase space (spinless) quasidensity for the ground state d_{gs} is obtained, as in the standard formalism, by integrating out one set of variables,

$$d_{\text{gs}}(\mathbf{r}; \mathbf{p}) = \frac{2}{\pi^3} \left(\frac{4\omega\mu}{(\omega + \mu)^2} \right)^{3/2} e^{-2r^2\omega\mu/(\omega+\mu)} e^{-2p^2/(\omega+\mu)}. \quad (6)$$

It is a simple exercise to recover from this Eq. (2–68) for $\rho_1(\mathbf{r}_1, \mathbf{r}'_1)$ in the treatment in [11]. The marginals of d_{gs} give the electronic density and momentum density.

It should be recognized that, while P_{gs} is a pure state, mathematically d_{gs} describes a mixed state. For Gaussians on phase space, such as P_{gs}

and d_{gs} too, there are simple rules to determine whether they represent a pure state [24], a mixed state [25], or neither. Writing $\mathbf{q} = (\mathbf{r}_1, \mathbf{r}_2)$, $\boldsymbol{\pi} = (\mathbf{p}_1, \mathbf{p}_2)$, $\mathbf{u} = (\mathbf{q}, \boldsymbol{\pi})$, we find $P_{\text{gs}}(\mathbf{u}) = \pi^{-6} e^{-\mathbf{u} \cdot F \mathbf{u}} = \pi^{-6} e^{-\mathbf{q} \cdot A \mathbf{q} - \boldsymbol{\pi} \cdot A^{-1} \boldsymbol{\pi}}$ where, amusingly,

$$A = \frac{1}{2} \begin{pmatrix} \omega + \mu & \omega - \mu \\ \omega - \mu & \omega + \mu \end{pmatrix}, \quad A^{-1} = \frac{1}{2} \begin{pmatrix} \omega^{-1} + \mu^{-1} & \omega^{-1} - \mu^{-1} \\ \omega^{-1} - \mu^{-1} & \omega^{-1} + \mu^{-1} \end{pmatrix}. \quad (7)$$

We see that the matrix F corresponding to formula (5) is symmetric and symplectic, and therefore represents indeed a pure state. This is not the case for d_{gs} . Thus our purpose in recovering P_{gs} from knowledge of d_{gs} *alone* is akin to putting Humpty Dumpty together again!

4 ... who traced these signs?

Since all the relevant quantities factorize, in this section we work in one dimension for notational simplicity. Write $u = (r, p)$. For the ground state on phase space formula (1) goes [19] into:

$$P_{\text{gs}}(u_1, u_2; \text{spin}) = \frac{(\uparrow_1 \downarrow_2 - \downarrow_1 \uparrow_2)(\uparrow_{1'} \downarrow_{2'} - \downarrow_{1'} \uparrow_{2'})}{2} \times \sum_{r,s=0}^{\infty} c_r c_s f_{rs}(u_1) f_{rs}(u_2), \quad (8)$$

where $c_r c_s = (\pm \sqrt{n_r})(\pm \sqrt{n_s})$, with the signs to be determined. The f_{rs} are Wigner eigentransitions, the functions on phase space corresponding to transitions between states. A similar series for triplet states is established and investigated in [26].

The explicit form of the f_{rs} will turn out to be well known. But first we have to find the good coordinates. According to a theorem in [25], the real quadratic form in the exponent of d_{gs} must be symplectically congruent to a diagonal one. We perform the transformation

$$(Q, P) := ((\omega\mu)^{1/4} r, (\omega\mu)^{-1/4} p); \quad \text{or, in shorthand,} \quad U = Su,$$

where S is symplectic. Introducing as well the parameter $\lambda := 2\sqrt{\omega\mu}/(\omega + \mu)$, the 1-quasidensity takes the simple form

$$d_{\text{gs}}(U) := d_{\text{gs}}(u(U)) = \frac{2\lambda}{\pi} e^{-\lambda U^2}.$$

From now on, we assume in the notation $\delta \geq 0$; the treatment for the “attractive” case $\omega < \mu$ follows parallel lines. Under that proviso, we may also write $\lambda =: \tanh(\beta/2)$, so that

$$\beta = \log \frac{1+\lambda}{1-\lambda} = 2 \log \frac{\sqrt{\omega} + \sqrt{\mu}}{\sqrt{\omega} - \sqrt{\mu}}, \quad \text{and} \quad \sinh(\beta/2) = \frac{\lambda}{\sqrt{1-\lambda^2}} = \frac{2\sqrt{\omega\mu}}{\omega - \mu}.$$

From the series formula,

$$\sum_{n=0}^{\infty} L_n(x) e^{-x/2} t^n = \frac{1}{(1-t)} e^{-x(1+t)/2(1-t)},$$

it follows that

$$d_{\text{gs}}(U) = \frac{4}{\pi} \sinh \frac{\beta}{2} \sum_{r=0}^{\infty} (-1)^r L_r(2U^2) e^{-U^2} e^{-(2r+1)\beta/2}.$$

One recognizes the basis of Wigner eigenfunctions on phase space corresponding to oscillator states [23]:

$$f_{rr}(U) = \frac{1}{\pi} (-1)^r L_r(2U^2) e^{-U^2}; \quad (9)$$

thus we realize that d_{gs} is in thin disguise a *Gibbs state* [25] with inverse temperature β :

$$d_{\text{gs}}(U) = 4 \sinh \frac{\beta}{2} \sum_{r=0}^{\infty} e^{-(2r+1)\beta/2} f_{rr}(U). \quad (10)$$

With this we have identified the natural orbitals in the U variables. Their occupation numbers are

$$\begin{aligned} n_r &= 2 \sinh \frac{\beta}{2} e^{-(2r+1)\beta/2} = \frac{4\sqrt{\omega\mu}}{\omega - \mu} \left(\frac{\sqrt{\omega} - \sqrt{\mu}}{\sqrt{\omega} + \sqrt{\mu}} \right)^{2r+1} \\ &= \frac{4\sqrt{\omega\mu}}{(\sqrt{\omega} + \sqrt{\mu})^2} \left(\frac{\sqrt{\omega} - \sqrt{\mu}}{\sqrt{\omega} + \sqrt{\mu}} \right)^{2r}. \end{aligned} \quad (11)$$

Notice that $n_0 = 1 - e^{-\beta} = Z^{-1}(\beta)$, for Z the system’s partition function; also $\sum_r n_r = (1 - e^{-\beta}) \sum_r e^{-r\beta} = 1$. These n_r have nice square roots:

$$\sqrt{n_r} = \frac{2(\omega\mu)^{1/4}}{\sqrt{\omega} + \sqrt{\mu}} \left(\frac{\sqrt{\omega} - \sqrt{\mu}}{\sqrt{\omega} + \sqrt{\mu}} \right)^r.$$

Finally, for $r \geq s$ one has [23]:

$$f_{rs}(U) := \frac{1}{\pi} (-1)^s \sqrt{\frac{s!}{r!}} (2U^2)^{(r-s)/2} e^{-i(r-s)\vartheta} L_s^{r-s}(2U^2) e^{-U^2},$$

where $\vartheta := \arctan(P/Q)$. The f_{sr} are complex conjugates of f_{rs} .

We turn now to the energy functionals, which should allow us to determine the correct signs in (8). Of course, still working in dimension one, the total energy in our units is just one half of the sum of the frequencies; and this is confirmed by the well-known formula for the Gibbs ensemble (consult [27] for the phase space derivation) represented by (10). To wit,

$$E_{\text{gs}} = E[d_{\text{gs}}] = 2\sqrt{\omega\mu} \left(\frac{1}{e^\beta - 1} + \frac{1}{2} \right) = \frac{\omega + \mu}{2}.$$

From the viewpoint of DFT, the most interesting part of the energy is the electron interaction $E_{2\text{gs}}$. The 1-body Hamiltonian is given by

$$h(u) = \frac{p^2}{2} + \frac{\omega^2 r^2}{2} = \sqrt{\omega\mu} \left(\frac{P^2}{2} + \frac{\omega Q^2}{2\mu} \right).$$

It is a simple exercise to obtain the 1-body energy $E_{1\text{gs}}$ by integrating expression (6) with this observable:

$$E_{1\text{gs}} = \frac{\omega}{2} + \frac{\mu^2 + \omega^2}{4\mu}.$$

It is easily checked that this equals $2 \sum_r n_r E_{rr}$, where E_{rr} denotes the 1-body energy associated to each natural orbital in (9). Thus it must be that

$$E_{2\text{gs}} = E_{\text{gs}} - E_{1\text{gs}} = \frac{\mu^2 - \omega^2}{4\mu}.$$

Now we go for the two-body contributions of the natural orbitals. The interelectronic repulsion potential in (3) is $(\mu^2 - \omega^2)r_{12}^2/4$, so they are of the form $\sum_{rs} c_r c_s L_{sr}$, with the L_{sr} given by:

$$\begin{aligned} L_{sr} &= \frac{\mu^2 - \omega^2}{4} \int f_{sr}(q_1; p_1) f_{sr}(q_2; p_2) (q_1 - q_2)^2 dq_1 dq_2 dp_1 dp_2 \\ &= \frac{\mu^2 - \omega^2}{4\sqrt{\omega\mu}} \int h_s(Q_1) h_r(Q_1) (Q_1 - Q_2)^2 h_s(Q_2) h_r(Q_2) dQ_1 dQ_2. \end{aligned}$$

Here h_r are the usual orthogonal harmonic oscillator eigenfunctions for unit frequency. We consider the diagonal $r = s$ first, whereby

$$L_{rr} = \frac{\mu^2 - \omega^2}{2\sqrt{\omega\mu}} \left(r + \frac{1}{2} \right); \quad \text{and thus}$$

$$\sum_r n_r L_{rr} = \frac{\mu^2 - \omega^2}{2\sqrt{\omega\mu}} \frac{4\sqrt{\omega\mu}}{(\sqrt{\omega} + \sqrt{\mu})^2} \frac{(\omega + \mu)(\sqrt{\omega} + \sqrt{\mu})^2}{16\omega\mu} = \frac{\mu^2 - \omega^2}{4\mu} \frac{\omega + \mu}{2\omega}.$$

We have used that the expected value of Q^2 for a harmonic oscillator eigenstate is $r + \frac{1}{2}$ and that the expected value of Q is zero. Notice that $\frac{\omega + \mu}{2\omega} < 1$. We have been considering $\mu < \omega$. For attraction between the electrons, this contribution changes sign.

A non-vanishing contribution of the off-diagonal part may then come only from the terms

$$\pm \frac{\omega^2 - \mu^2}{2\sqrt{\omega\mu}} \sqrt{n_r n_{r+1}} \left[\int h_r(Q) h_{r+1}(Q) Q dQ \right]^2.$$

We compute:

$$\begin{aligned} & \frac{\omega^2 - \mu^2}{\sqrt{\omega\mu}} \sum_{r=0}^{\infty} \sqrt{n_r n_{r+1}} \left[\int h_r(Q) h_{r+1}(Q) Q dQ \right]^2 \\ &= \frac{\omega^2 - \mu^2}{\sqrt{\omega\mu}} \frac{4\sqrt{\omega\mu}(\sqrt{\omega} - \sqrt{\mu})}{(\sqrt{\omega} + \sqrt{\mu})^3} \sum_{r=0}^{\infty} \left(\frac{\sqrt{\omega} - \sqrt{\mu}}{\sqrt{\omega} + \sqrt{\mu}} \right)^{2r} \frac{r+1}{2} \\ &= (\omega^2 - \mu^2) \frac{2(\sqrt{\omega} - \sqrt{\mu})}{(\sqrt{\omega} + \sqrt{\mu})^3} \frac{(\sqrt{\omega} + \sqrt{\mu})^4}{16\omega\mu} = \frac{\omega^2 - \mu^2}{4\mu} \frac{\omega - \mu}{2\omega}. \end{aligned}$$

Here we employ $\sum_{r=0}^{\infty} (r+1)x^r = (1-x)^{-2}$. The factor $(r+1)/2$ comes from the definition of the emission operators $a^\dagger = (Q - iP)/\sqrt{2}$ (or the absorption operators), with $a^\dagger h_r = \sqrt{r+1} h_{r+1}$. There is also an overall factor of 2 coming from two subdiagonals for each r . Obviously there are no other contributions.

In conclusion, to minimize the energy we now have to choose *minus* signs whenever $s = r \pm 1$. This conclusion does not depend on whether the electrons attract or repel each other. It determines all the signs in (8). Then the total 2-body energy comes out as

$$\frac{\mu^2 - \omega^2}{4\mu} \frac{\omega + \mu}{2\omega} - \frac{\omega^2 - \mu^2}{4\mu} \frac{\omega - \mu}{2\omega} = \frac{\mu^2 - \omega^2}{4\mu},$$

as it ought to be.

Theorem 1. *The ground state of harmonium is equal to*

$$P_{\text{gs}}(u_1, u_2) = (-)^{r+s} \sqrt{n_r n_s} f_{rs}(u_1) f_{rs}(u_2),$$

where the f_{rs} are the oscillator eigentransitions up to a symplectic change of basis, and the n_r have been given in (11).

According to the spirit of DFT, the above result has been derived from knowledge of d_{gs} alone; the advantage of working with Wigner distributions being that the necessary transformations are completely transparent. However, since we had P_{gs} explicitly beforehand, it is nice to make the check. In (8) sum over each subdiagonal, where $r - s = l \geq 0$:

$$\begin{aligned} \sum_{r-s=l} \sqrt{n_r n_s} f_{rs}(u_1) f_{rs}(u_2) &= \frac{n_0}{\pi^2} e^{-l\beta/2} (2U_1 U_2)^l e^{-il(\vartheta_1 + \vartheta_2)} e^{-U_1^2 - U_2^2} \\ &\times \sum_{s=0}^{\infty} \frac{s!}{(l+s)!} e^{-s\beta} L_s^l(2U_1^2) L_s^l(2U_2^2) = \frac{e^{-(U_1^2 + U_2^2)/\lambda}}{\pi^2} e^{-il(\vartheta_1 + \vartheta_2)} I_l\left(\frac{2U_1 U_2}{\sinh(\beta/2)}\right), \end{aligned}$$

where I_l is the modified Bessel function. The generating function identity

$$I_0(z) + 2 \sum_{l=1}^{\infty} I_l(z) \cos(l\theta) = e^{z \cos \theta},$$

where the sign rule dictates $\theta = \vartheta_1 + \vartheta_2 + \pi$, yields for the total sum:

$$\begin{aligned} &\pi^{-2} e^{-[(U_1^2 + U_2^2)/\lambda + 2U_1 U_2 \operatorname{csch}(\beta/2) \cos(\vartheta_1 + \vartheta_2)]} \\ &= \pi^{-2} e^{-\frac{1}{2}[(r_1^2 + r_2^2)(\omega + \mu) + (p_1^2 + p_2^2)(\omega^{-1} + \mu^{-1})]} e^{-r_1 r_2 (\omega - \mu)} e^{p_1 p_2 (\mu^{-1} - \omega^{-1})}, \end{aligned} \quad (12)$$

which is the correct result. To our knowledge this the first analytical verification of the two-electron state theorem.

Once the correct sign configuration in the functional is obtained, one may compare it with standard approximate workhorses like the Müller functional [8, 28]. Müller's is a clever variation on the standard Hartree–Fock functional. For a two-electron system in the phase space approach, it adopts instead of (8) the form:

$$\begin{aligned} P_{\text{M}}(u_1, u_2; \text{spin}) &= \frac{1}{2} (\uparrow_1 \downarrow_2 - \downarrow_1 \uparrow_2) (\uparrow_{1'} \downarrow_{2'} - \downarrow_{1'} \uparrow_{2'}) \\ &\times \left(\sum_{r,s=0}^{\infty} n_r n_s f_{rr}(u_1) f_{ss}(u_2) - \sum_{r,s=0}^{\infty} \sqrt{n_r n_s} f_{rs}(u_1) f_{sr}(u_2) \right). \end{aligned}$$

It is well known that for Coulombian systems the Müller functional tends to overbind. The rigorous proof of this fact for real two-electron atoms given in [19] is much more transparent than the one in [28]; it shows that definite positivity of the Coulomb potential does play a decisive role, whereas the extra minus signs in Müller's functional do not. For these very reasons the Müller functional's tendency to overcorrelate needs reexamination in harmonium. This is taken up in [26].

5 On the correlation functional

The Wigner quasiprobability for the best Hartree–Fock state for harmonium is given by

$$\begin{aligned} P_{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{p}_1, \mathbf{p}_2) &= \frac{1}{\pi^6} e^{-(r_1^2 + r_2^2)\sqrt{(\omega^2 + \mu^2)/2}} e^{-(p_1^2 + p_2^2)/\sqrt{(\omega^2 + \mu^2)/2}} \\ &= \frac{1}{\pi^6} e^{-(R^2 + r^2)\sqrt{(\omega^2 + \mu^2)/2}} e^{-(P^2 + p^2)/\sqrt{(\omega^2 + \mu^2)/2}}. \end{aligned}$$

We refer to [10] for the derivation of the Hartree–Fock wave function for harmonium, from which the above follows by (4). From the above, comparing with the exact state under the form (5) or (12), a “Moshinsky hole” in phase space is clearly visible.

The correlation energy E_c is defined as the difference between the true energy of the electronic system and the Hartree–Fock energy. For harmonium, use of P_{HF} gives

$$\begin{aligned} E_{\text{HF}} &= \frac{1}{\pi^6} \int \left(\frac{P^2}{2} + \frac{\omega^2 R^2}{2} + \frac{p^2}{2} + \frac{\mu^2 r^2}{2} \right) \\ &\quad \times e^{-(R^2 + r^2)\sqrt{(\omega^2 + \mu^2)/2}} e^{-(P^2 + p^2)/\sqrt{(\omega^2 + \mu^2)/2}} d^3 \mathbf{P} d^3 \mathbf{R} d^3 \mathbf{p} d^3 \mathbf{r} \\ &= \frac{3\sqrt{(\omega^2 + \mu^2)/2}}{4} + \frac{3\omega^2}{4\sqrt{(\omega^2 + \mu^2)/2}} + \frac{3\sqrt{(\omega^2 + \mu^2)/2}}{4} + \frac{3\mu^2}{4\sqrt{(\omega^2 + \mu^2)/2}} \\ &= 3\sqrt{(\omega^2 + \mu^2)/2}, \end{aligned}$$

and so the correlation energy is

$$E_c := E_0 - E_{\text{HF}} = 3 \left(\frac{\omega + \mu}{2} - \sqrt{\frac{\omega^2 + \mu^2}{2}} \right) \sim -\frac{3\delta^2}{32\omega^3},$$

as $\delta \downarrow 0$ keeping ω fixed, or as $\omega \uparrow \infty$ keeping δ fixed. If we understand the latter as the “high-density” limit, the correlation energy vanishes in it. In [29] the high energy limit is understood as the limit $\mu \uparrow \infty$, with ω kept constant. In both cases the behaviour of correlation is at variance with that of the Coulomb potential [30].

As indicated in the introduction, Gill’s program for the correlation energy [14, 31] is based exclusively on the Wigner intracule. Since relative momentum is as important as relative position in determining interelectronic correlation, it is certainly appealing to study correlation on phase space. More precisely, the full Wigner distribution is reduced to the relative variables $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$, $\mathbf{p}_{12} = \mathbf{p}_1 - \mathbf{p}_2$. Then it is conjectured that the correlation energy is a universal functional of the “Omega intracule” Ω , that is, the intracule on phase space after reduction to the variables r_{12}, p_{12}, w , with w the angle between \mathbf{r}_{12} and \mathbf{p}_{12} , of the form:

$$E_c = \int_0^\infty \int_0^\infty \int_0^\pi \Omega(r_{12}, p_{12}, w) G(r_{12}, p_{12}, w) dw dp_{12} dr_{12};$$

or even a functional of the lower intracules:

$$E_c = \int_0^\infty \int_0^\infty W(r_{12}, p_{12}) G(r_{12}, p_{12}) dp_{12} dr_{12}; \quad E_c = \int_0^\infty A(s) G(s) ds,$$

with $s := r_{12}p_{12}$. In our case, recalling $\mathbf{r} = \mathbf{r}_{12}/\sqrt{2}$, $\mathbf{p} = \mathbf{p}_{12}/\sqrt{2}$, the exact intracule takes the form

$$\frac{1}{\pi^3} e^{-\mu r^2 - p^2/\mu} \longrightarrow \frac{2}{\pi} r_{12}^2 p_{12}^2 e^{-\mu r_{12}^2/2} e^{-p_{12}^2/2\mu} =: W_{\text{ex}}(r_{12}, p_{12}),$$

after integration over the angles. While the Hartree-Fock intracule is:

$$\frac{2}{\pi} r_{12}^2 p_{12}^2 e^{-\sqrt{(\omega^2 + \mu^2)/2} r_{12}^2/2} e^{-p_{12}^2/2\sqrt{(\omega^2 + \mu^2)/2}} =: W_{\text{HF}}(r_{12}, p_{12});$$

which, as observed in [29], is of the same form as the exact one when replacing δ by $\delta/2$. As a consequence the “action intracules”:

$$A(s) = \frac{2}{\pi} \int_0^\infty r_{12}^2 \frac{s^2}{r_{12}^2} e^{-\bullet r_{12}^2/2} e^{-s^2/2\bullet r_{12}^2} \frac{dr_{12}}{r_{12}} = \frac{2s^2}{\pi} K_0(s)$$

for any value of \bullet , are precisely the same for the exact and Hartree-Fock cases. Note that in the exact solution only the intracule part of the Wigner quasiprobability changes in harmonium, while the Hartree-Fock method modifies both the extracule and the intracule; and then both contribute to the correlation energy. However, in Gill’s W -functions the footprints of both harmonium frequencies are jointly kept.

6 Conclusion and outlook

We have beaten a path from Schmidt series to the exact energy functional for two-electron systems, and fully determined the latter for the harmonium model of an atom, by working with Wigner distributions on phase space. We hope this paper helps to understand why this kind of approach is bound to grow in importance in the coming years.

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